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Continuous measurements of stable carbon isotopes in CO_2 with a near-IR laser absorption spectrometer

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HIGHLIGHTS

- We measured stable carbon isotope ratios of CO_2 by a laser absorption spectrometer.
- The H_2O broadening coefficients of CO_2 were determined.
- The effect of humidity on $\delta^{13}C$ determination was examined.
- The spectrometer keeps constant measurement conditions over 12-h periods.

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ABSTRACT

A near-IR laser absorption spectrometer using a technique of wavelength modulation spectroscopy is used to measure stable carbon isotope ratios of ambient CO_2 ($\delta^{13}C$) via the absorption lines $^{12}CO_2$ R(17) $(2\nu_1 + \nu^1{}_2 - \nu^1{}_2 + \nu_3)$ at 4978.205 cm^{-1} and $^{13}CO_2$ P(16) $(\nu_1 + 2\nu_2 + \nu_3)$ at 4978.023 cm^{-1}. The isotope ratios are measured with a reproducibility of 0.02‰ (1σ) in a 130-s integration time over a 12-h period. The humidity effect on $\delta^{13}C$ values has been evaluated in laboratory experiments. The $\delta^{13}C$ values of CO_2 in ambient air were measured continuously over 8 days and agreed well with those from isotope ratio mass spectrometry of canister samples. The spectrometer is thus capable of real-time, *in situ* measurements of stable carbon isotope ratios of CO_2 under ambient conditions.

1. Introduction

Precise measurements of the stable carbon isotopes of atmospheric carbon dioxide (CO_2) provide important information about carbon exchange processes. This is due to the differences in the isotope ratios among various sources and sinks of CO_2, such as plant respiration, photosynthesis, anthropogenic and marine impacts [1], all of which are generated by chemical reactions and/or biogeochemical processes. The isotope ratio $^{13}C/^{12}C$ is typically expressed relative to a standard reference through the formula.

$$\delta^{13}C = \left(\frac{R^{13}_{sample}}{R^{13}_{reference}} - 1\right) \times 1000 \qquad (1)$$

where R^{13} is the ratio $^{13}C/^{12}C$. The $\delta^{13}C$ value is usually reported in per mil (‰) relative to the international PDB-standard reference (Belemnite of the Pee Dee Formation in South Caroline, $[^{13}C]/[^{12}C] = 0.011237$) [2]. Isotope ratio mass spectrometry (IRMS) is the standard analytical method for the determination of isotope ratios [3], with a measurement precision from 0.01‰ to 0.1‰. In most cases, however, collected field samples must be analyzed in the laboratory. IRMS has other experimental drawbacks such as in the great care needed for sample preparation involving chemical processing or purification [4]. Thus high precision, *in situ* measurements of isotope ratios in the field would be advantageous.

Infrared absorption spectroscopy has been used to measure stable isotopes ratios for molecules having following three features: (1) The ro-vibronic absorption lines are well resolved to prevent spectral interference by own and other species absorption lines. (2) The absorption lines lie within a common scan window. (3) The intensities of the absorption lines of stable isotopes are almost identical and the linearity of the intensity is kept to avoid saturation and nonlinear effects by the detectors [5]; in these ways, specific isotopes can be quantified. Mid-infrared and near-infrared spectroscopic techniques such as Fourier transform infrared (FT-IR) spectroscopy [6,7] with a White-type multi-pass cell, and absorption spectroscopy with lead-salt tunable diode lasers (TDL) and

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an astigmatic Herriott-type multi-pass cell [8] have been applied to isotope ratio analysis. The FTIR measurements reached a maximum precision for $\delta^{13}C$ of 0.15‰ due to the optimization of FTIR spectra analysis [7]. However, since both FT-IR and mid-infrared TDL require cryogenic cooling, they are not suitable for long-term *in situ* measurements. A direct absorption technique with a light source at 4.3 μm, based on difference-frequency generation (DFG), was shown to achieve 0.8‰ precision for $\delta^{13}C$ at an ambient level of CO_2 [5]. An improvement of the mid-IR laser source will enable high precision measurement of stable carbon isotopes of CO_2 [5]. The quantum cascade laser (QCL), which requires thermoelectric cooling and has high spectral purity, has been used for detection of ambient CO_2 stable isotopes in the 4.3 μm region [9–15] with less than 0.1‰ precision [12]. In this wavelength region, measurements of stable oxygen isotopes were reported as well [12–15]. Thus QCL systems have been used for field measurements of both carbon and oxygen isotope ratios [13–15].

In the near-infrared region, relatively low-cost, compact-sized distributed feedback (DFB) lasers are available. Since they have a narrow bandwidth and a relatively high power output, they are well suited for a compact isotope analyzer. However, since absorption cross-sections of CO_2 at 1.6 μm are a factor of 10^4 smaller than those in the 4.3 μm region, highly sensitive spectroscopic techniques are required, such as wavelength modulation spectroscopy (WMS) and cavity ring-down spectroscopy (CRDS) [16–19]. In the 1.6 μm region, stable carbon isotopes of CO_2 were probed with CRDS [16]. In the 2 μm region, where the CO_2 absorption cross-sections are 100 times larger than those in the 1.6 μm region, stable carbon isotopes were measured with WMS [17–19] and off-axis cavity-enhanced absorption spectroscopy [20]. In the 2 μm region, the best precision among the literature was 0.3‰ at 2% of CO_2 [17].

Although continuous field measurements of $\delta^{13}C$ in ambient CO_2 are becoming possible with the laser spectroscopic techniques mentioned above [12–15], the effect of humidity on the data has not been evaluated in detail. Since ambient humidity varies significantly, there is a possibility that spectral overlap by H_2O lines and/or spectral broadening of CO_2 by H_2O can have an influence on the $\delta^{13}C$ results. Data on air, N_2, and O_2 broadening parameters of CO_2 are available in the 1.42–2.32 μm region [21,22]. H_2O broadening coefficients of some CO_2 absorption lines have been reported at 4.3 μm [23] and at 1.57 μm [24]. However, to our knowledge, there are no reported data for the 2 μm region.

Recently, our group has developed a near-IR laser absorption spectrometer that uses a 2.008 μm DFB laser [25]. The spectrometer made it possible to measure isotope ratios ($\delta^{13}C$) for 346.6 ppm CO_2 with a reproducibility of 0.24‰ (1σ) over a 130-s integration time for 10-h period [25]. For the present work, we had two major objectives. First, we evaluated the humidity effect on $\delta^{13}C$ determination. Since there is no spectral overlap between H_2O lines and the CO_2 absorption line pair selected for the $\delta^{13}C$ determination [25], it was necessary to evaluate the effect of spectral broadening of the CO_2 lines by H_2O. This is especially important because $\delta^{13}C$ is determined by the WMS signal intensity, which is the difference between the peak intensity and the baseline [25]; thus pressure broadening of the $^{12}CO_2$ and $^{13}CO_2$ spectra by H_2O affects the $\delta^{13}C$ determination. The H_2O broadening coefficients of the $^{12}CO_2$ and $^{13}CO_2$ absorption line pairs in the 2 μm region were obtained independently by direct absorption spectroscopy of pure $^{12}CO_2$ and $^{13}CO_2$ samples. The second objective was to provide continuous measurements of outside air at The University of Tokyo in central Tokyo. In order to assess the performance of our instruments, CO_2 mixing ratios in outside air were compared with those measured using a non-dispersed infrared spectrometer (NDIR). In addition, $\delta^{13}C$ values were compared with those from canister samplings analyzed by IRMS.

2. Experiments

2.1. Near-IR laser absorption spectrometer and H_2O broadening coefficient measurements

Our instrument is based on WMS using a 2.008 μm DFB laser and a Herriot-type multi-pass cell, as described previously [25]. The absorption line pair for the measurements of the stable carbon isotope ratio was $^{12}CO_2$ R(17) ($2\nu_1 + \nu^1_2 - \nu^1_2 + \nu_3$, 4.47×10^{-23} cm^2 $molecule^{-1}$ cm^{-1}) at 4978.205 cm^{-1} and $^{13}CO_2$ P(16) ($\nu_1 + 2\nu_2 + \nu_3$, 7.07×10^{-24} cm^2 $molecule^{-1}$ cm^{-1}) at 4978.023 cm^{-1} [25]. The injection current and the laser-chip temperature of the 10 mW, 2.008-μm single-mode DFB laser diode (NTT Electronics, Yokohama, Japan) were maintained with a diode laser control unit (ILX LDC3724C ILX Lightwave, Bozeman, MT, USA). The beam was collimated with an anti-reflection (AR) coated lens (Schäfter + Kirchhoff 60FC-4-A11–09, Hamburg, Germany) and introduced into a wedged-window, Herriott-type multi-pass cell. The laser beam was focused in the center of the cell with a 500 mm AR-coated CaF_2 lens. The optical path length in the cell was 29.91 m and the cell volume was 0.9 L. The transmitted laser beam was detected by an InGaAs photodiode (THORLABS PDA10DT, Newton, NJ, USA).

The laser was scanned at 0.77 Hz, which was controlled by a triangle voltage wave supplied by a function generator (Agilent 33220A, Santa Clara, CA, USA). The modulation frequency was set to 11 kHz using the reference output of a digital lock-in amplifier (Stanford Research Systems SR810, Sunnyvale, CA, USA). The signal from the photodetector was processed by the lock-in with a time constant of 3-ms and 24-dB/oct digital filtering, corresponding to an equivalent noise bandwidth of 26 Hz. The modulation conditions were adjusted to obtain the highest signal-to-noise ratio (S/N) for the second harmonic of the WMS signals of $^{12}CO_2$. The data was acquired in a laptop PC through a 16-bit AD PCMCA card (CONTEC ADA16-8/2(CB)L, Osaka, Japan).

The multi-pass cell was evacuated either with a rotary pump through a liquid-nitrogen trap or with a dry pump. The pressure was monitored using a capacitance manometer (MKS Baratron 722B, Andover, MA, USA) and controlled to within 0.01 kPa by mass flow controllers (Kofloc 3660, Kyoto, Japan) positioned before and after the cell. The temperature was controlled to within ±0.01 K. All experiments except for the measurements of H_2O broadening coefficients were performed at 313 K. The DFB laser, the optics and the cell were placed in an N_2-purged box.

The standard gas used was (i) synthetic air (CO_2 366 ppm, $\delta^{13}C = -34.5$‰), (ii) compressed air (CO_2 393 ppm, $\delta^{13}C = -10.5$‰), (iii) compressed air (CO_2 424 ppm, $\delta^{13}C = -11.6$‰), (iv) compressed air (432 ppm CO_2, $\delta^{13}C = -12.9$‰). The synthetic air cylinder was purchased from Taiyo Nippon Sanso Corp, Tokyo, Japan. The compressed air cylinders were purchased from Suzuki Shokan Corp, Tokyo, Japan.

The selected line pair meets the requirements for the quantitative measurements of stable carbon isotopes of CO_2 shown in the introduction section. The signal intensities as a function of mixing ratio at ambient levels of CO_2 are shown in Fig. 1, suggesting that the linearity of the signal intensity is kept.

To assess signal stability, compressed air (393 ppm CO_2) was introduced into the WMS system with a flow rate of approximately 115 sccm (standard cc per minute). The pressure and the temperature were maintained at 10 kPa and 313 K, respectively. The instrument performance was tested using the Allan variance method [26]. The signal intensity ratio of $I(^{13}CO_2)/I(^{12}CO_2)$ was measured with 0.77 Hz resolution over 5 h. Results are shown in Fig. 2, where the $I(^{13}CO_2)/I(^{12}CO_2)$ time series and the associated Allan variance (σ_A^2) are plotted. From the Allan variance plot, an optimum integration time of 100–200 s with $\sigma_A^2 = 1.4 \times 10^{-6}$ can